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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Catalysts with Fine-Particle Dispersion of the Active Component

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Notice: This application is as filed and may therefore contain an incomplete specification.





**PCT**  
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<p>(51) Internationale Patentklassifikation <sup>5</sup> : <b>B01J 23/00, C07C 29/154</b></p>	<p><b>A1</b></p>	<p>(11) Internationale Veröffentlichungsnummer: <b>WO 94/16815</b></p> <p>(43) Internationales Veröffentlichungsdatum: <b>4. August 1994 (04.08.94)</b></p>
<p>(21) Internationales Aktenzeichen: <b>PCT/EP94/00083</b></p> <p>(22) Internationales Anmeldedatum: <b>13. Januar 1994 (13.01.94)</b></p> <p>(30) Prioritätsdaten: <b>P 43 01 469.0      21. Januar 1993 (21.01.93)      DE</b></p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): <b>BASF AKTIENGESellschaft [DE/DE]; D-67056 Ludwigshafen (DE).</b></p> <p>(72) Erfinder; und</p> <p>(75) Erfinder/Anmelder (nur für US): <b>FETZER, Thomas [DE/DE]; Wormser Landstrasse 144, D-67346 Speyer (DE). BUECHELE, Wolfgang [DE/DE]; An der Froschlache 7, D-67063 Ludwigshafen (DE). IRGANG, Matthias [DE/DE]; Andreas-Hofer-Weg 41, D-69121 Heidelberg (DE). OTTO, Bernhard [DE/DE]; Albert-Schweitzer-Strasse 1, D-67117 Limburgerhof (DE). WISTUBA, Hermann [DE/DE]; Mudauer Ring 227, D-68259 Mannheim (DE). BUERGER, Gert [DE/DE]; Hoefnerstrasse 16, D-68199 Mannheim (DE).</b></p> <p>(74) Gemeinsamer Vertreter: <b>BASF AKTIENGESellschaft; Patentabteilung ZDX-C6, D-67056 Ludwigshafen (DE).</b></p>	<p style="text-align: right; font-size: 1.2em; font-weight: bold;">2152815</p> <p>(81) Bestimmungsstaaten: <b>AU, BB, BG, BR, BY, CA, CN, CZ, FI, HU, JP, KP, KR, KZ, LK, LV, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, UZ, VN, europäisches Patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI Patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Veröffentlicht</b> <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i></p>	
<p>(54) Title: <b>CATALYSTS WITH HIGHLY DISPERSED ACTIVE COMPONENTS</b></p> <p>(54) Bezeichnung: <b>KATALYSATOREN MIT HOCHDISPERSER VERTEILUNG DER AKTIVKOMPONENTE</b></p> <p>(57) Abstract</p> <p>Catalysts are produced by combining <math>M-Al_2O_4</math>, in which M stands for an element of the I, VII and VIII secondary groups of the periodic table of elements, with tin, lead, an element of the II main or secondary group of the periodic table of elements, as an oxide or salt or in its elementary form, and by calcinating them at temperatures from 300 to 1300 °C and pressures from 0.1 to 200 bars. Also disclosed is a process for producing these catalysts.</p> <p>(57) Zusammenfassung</p> <p>Katalysatoren hergestellt durch Vereinigung von <math>M-Al_2O_4</math>, wobei M für ein Element der I., VII. und VIII. Nebengruppe des Periodensystems der Elemente steht, mit Zinn, Blei, einem Element der II. Haupt- oder Nebengruppe des Periodensystems der Elemente als Oxid oder Salz oder in elementarer Form und Calcinieren bei Temperaturen von 300 bis 1300 °C und Drücken von 0,1 bis 200 bar sowie das Verfahren zu ihrer Herstellung.</p>		

Catalysts with fine-particle dispersion  
of the active component

The present invention relates to catalysts with fine-particle dispersion of the active component and to  
5 a process for preparing these catalysts.

WO-A-89/00082 and the citations given therein describe the preparation of oxide catalysts which contain Cu, Zn and Al, employing as precursor a Cu-An-Al alloy which is partly or completely converted into the oxide in  
10 an oxidation step. The catalysts are employed for preparing methanol.

DE-A-37 17 111 discloses a process for preparing a copper-containing catalyst for low-temperature shift conversion which, besides copper oxide, also contains  
15 zinc oxide and aluminum oxide. The catalyst is prepared by precipitation of the water-soluble salts from aqueous solution using an alkaline precipitant.

The known catalysts are unsatisfactory in respect of useful life and activity.

20 It is an object of the present invention to remedy the abovementioned disadvantages.

We have found that this object is achieved by novel and improved catalysts prepared by combining  $M-Al_2O_3$ , where M is an element of Group Ib, VIIb or VIII of the  
25 Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.

The catalysts according to the invention can be  
30 prepared as follows:

The starting material may be a solid oxide which is wholly or partly, ie. 1-100%, preferably 10-90%, particularly preferably 20-70%, by weight, a spinel of the composition  $M-Al_2O_3$  in an  $Al_2O_3$  matrix, and this can be  
35 mixed with the same or higher concentration of tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements, as oxide or salt or in elemental form, and

calcined at 300-1300°C, preferably 500-1200°C, particularly preferably 600-1100°C, under 0.1-200 bar, preferably 0.5-10 bar, particularly preferably under atmospheric pressure.

5           The mixing can take place, for example, by spraying, mechanical mixing, stirring or kneading the ground solid of the composition  $M\text{-Al}_2\text{O}_4$ , preferably in  $\text{Al}_2\text{O}_3$ , particularly preferably in  $\gamma\text{-Al}_2\text{O}_3$ , or preferably by impregnating an unground solid of the composition  $M\text{-Al}_2\text{O}_4$ ,  
10 preferably in  $\text{Al}_2\text{O}_3$ , particularly preferably in  $\gamma\text{-Al}_2\text{O}_3$ , with a solution of salts of tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements.

          The liberation of the element M in the form of the element or oxide, which as a rule leads to fine-  
15 particle dispersion, can be induced by replacing the element M in the spinel in the calcination step by tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements, in the form of the element, oxide or salt-like compound when the resulting spinel is more  
20 thermodynamically stable than the original spinel  $M\text{-Al}_2\text{O}_4$ .

          Suitable as metal M in the starting oxides  $M\text{-Al}_2\text{O}_4$  are elements of group Ib, VIIb and VIII of the Periodic Table of the Elements in the +2 oxidation state, such as  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ , especially  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  or  
25 mixtures thereof.

          The elements of group IIa or IIb of the Periodic Table of the Elements can be used in the form of the metal, oxides or salt-like compounds. Examples of salt-like compounds are carbonates, hydroxides, carboxylates,  
30 halides and oxo anions such as nitrates, nitrites, sulfites, sulfates, phosphites, phosphates, pyrophosphates, halites, halates and basic carbonates, preferably carbonates, hydroxides, carboxylates, nitrates, nitrites, sulfates, phosphates and basic carbonates, particularly  
35 preferably carbonates, hydroxides, basic carbonates and nitrates, preferably in the +2 oxidation state such as  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , especially  $\text{Zn}^{2+}$  and  $\text{Mg}^{2+}$  or

mixtures thereof.

The preparation of the starting oxide of the composition  $M-Al_2O_3$ , preferably in the form of a spinel, is disclosed in, for example, WO-A-82/00820, 5 SU-A-426 968, FR-A-2 655 878 and Rev. Chim. 20 (1969) 105-106. It proves advantageous to impregnate an  $Al_2O_3$  carrier with a soluble compound such as a salt of the cation M, eg. a nitrite, nitrate, sulfite, sulfate, carbonate, hydroxide, carboxylate, halide, halite or 10 halate, and subsequently to decompose the anion to the oxide thermally. Another possibility comprises mixing a compound such as a salt of the cation M with an oxygen-containing aluminum compound, eg. by drying or in suspension, especially by spray-drying, compacting the 15 material, eg. by kneading, where appropriate by adding a suitable molding aid, molding by extrusion, drying and subsequently calcining to form the spinel. The calcination can be carried out at 300-1300°C, preferably 600-1000°C.

20 Doping of aluminum oxide carriers with a large surface area, ie. the formation of mixed oxides, increases the thermal stability of the carrier (eg. DE-A-34 03 328, DE-A-25 00 548, Appl. Catal. 7 (1983) 211-220, J. Catal. 127 (1991) 595-604). The foreign ions 25 may additionally contribute to the catalytic activity of the catalyst. The following elements may be generally employed for the doping: alkali metals, rare earth metals, Sc, Ti, V, Cr, Y, Zr, B, Si, Ge, P, Bi. The degree of replacement of aluminum oxide can be, for 30 example, 0.01-20% by weight.

The particle size of the oxide of the metal M in the unused catalyst is 1-200 nm, preferably 3-100 nm, particularly preferably 10-50 nm. The particle size can be determined, for example, by XRD (X-ray diffraction) or 35 TEM (transmission electron microscopy).

The catalysts according to the invention contain mesopores of 2-20 nm and macropores of more than 20 nm

and have BET surface areas of 1-350 m<sup>2</sup>/g, preferably 10-200 m<sup>2</sup>/g, particularly preferably 25-150 m<sup>2</sup>/g, and porosity of 0.01-0.8 ml/g.

The catalysts according to the invention are  
5 suitable, for example, for CO conversion and for methanol synthesis.

#### EXAMPLES

##### Preparation of the catalyst

##### EXAMPLE 1

10 A mixture of 284 g of Puralox® SCF (from Condea), 166 g of Pural® SB (from Condea) and 100 g of CuO (from Merck) was kneaded with 20 ml of formic acid (dissolved in 140 ml of H<sub>2</sub>O) for 0.75 h, extruded to 3 mm extrudates, dried and calcined at 800°C for 4 h.

15 A CuAl<sub>2</sub>O<sub>4</sub>-containing solid with a BET surface area of 112 m<sup>2</sup>/g and a bimodal pore radius distribution with a diameter of 25% of the pores being in the range 10-1 micrometers and of 65% of the pores being in the range 20-5 nanometers was obtained.

20 71.4 g of the CuAl<sub>2</sub>O<sub>4</sub>-containing solid (water uptake: 69.1%) were impregnated twice with 49 ml of an aqueous solution which contained nitric acid (pH 3) and 32.6 g of Zn(NO<sub>3</sub>)<sub>2</sub> and then left at room temperature for one hour. The impregnated carrier was dried to constant  
25 weight at 120°C and finally calcined at 600°C for 4 h.

A ZnAl<sub>2</sub>O<sub>4</sub>-containing solid with a BET surface area of 82 m<sup>2</sup>/g and an unchanged bimodal pore radius distribution was obtained with formation of CuO.

The size of the copper oxide crystallites was  
30 determined using X-rays and is 28 nm.

We claim:

1. A catalyst prepared by combining  $M-Al_2O_3$ , where M is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group  
5 IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.
2. A process for preparing catalysts, which comprises combining oxides of the formula  $M-Al_2O_3$ , where M is  
10 an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.
- 15 3. A process for preparing catalysts as claimed in claim 2, wherein the substituent M in the oxides  $M-Al_2O_3$  is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements.
4. A process for preparing catalysts as claimed in  
20 claim 2, wherein zinc, magnesium, calcium, strontium or barium is used as oxide or salt or in elemental form.
5. A process for preparing catalysts as claimed in claim 2, wherein the compounds of the elements of Group Ib, VIIb and VIII of the Periodic Table of the Elements  
25 are oxides of manganese, iron, cobalt, nickel or copper.